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(54) Title: SUPPORTED IONIC TRANSITION METAL CATALYSTS FOR OLEFIN POLYMERIZATION (57) Abstract A supported catalyst for olefin polymerization comprising a monocyclopentadienyl Group 4 transition metal component, an ionic activator component comprising a cation capable or irreversibly reacting with a ligand of the transition metal component and a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 angstroms, and a support material.		

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SUPPORTED IONIC TRANSITION METAL CATALYSTS FOR OLEFIN POLYMERIZATION

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Background of the Invention

1. Field of the Invention

10 The invention relates to supported ion-exchange catalysts useful for polymerization of olefins, diolefins, cyclic olefins and acetylenically unsaturated monomers.

2. Background

15

European Patent Application 277,003, 277,004 and PCT International Application WO 92/00333 describe an advance in Group 4 transition metal catalysts; a new catalyst which does not require either an alkyl aluminum or alumoxane as an activator. The Group 4 transition metal catalyst is prepared
20 as a reaction product of a transition metal compound and an ionic activator compound. The ionic activator comprises a cation which will irreversibly react with at least one ligand contained in Group 4 metal compound and a labile, bulky (approximately 4 angstroms or larger) anion which is a single coordination complex having a plurality of lipophilic radicals covalently
25 coordinated to and shielding a central charge-bearing metal or metalloid atom, the bulk of said anion being such that upon reaction, the activator is sterically hindered from covalently coordinating to the metal cation. Hence an active catalytic species of a transition metal is formed, namely an ionic pair comprising a transition metal cation paired with the noncoordinating anion of
30 the activator component.

The new transition metal catalyst system (hereafter referred to as an "ionic catalyst") eliminates the need for an expensive alumoxane activator. The ionic catalyst also offers other advantages over the alumoxane activated
35 catalysts such as: (1) high weight average molecular weight; (2) high catalytic activity; (3) good incorporation of comonomers; and (4) the control of the chain end chemistry of the polymer.

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Homogeneous ionic catalyst generally cannot be practically used for gas phase polymerization. The use of a supported catalyst offers the possibility of gas phase compatibility. Control of the particle size distribution of the polymeric product in the various polymerization processes eliminates or reduces the extent of reactor fouling.

Supported catalyst for olefin polymerization are well known in the art. These catalysts offer, among others, the advantages of being usable in gas or slurry phase reactors, allowing the control of polymer particle size and thereby the control of product bulk density. Gas phase reactors also eliminate the need for a solvent and the equipment for solvent handling the separation. However, the known Ziegler-Natta olefin polymerization supported catalysts also present disadvantages which include broad MWD and broad CD, inefficient incorporation of comonomers, poor sequence distribution and, in the case of lower activity catalysts, the need for a product deashing step.

Supported transition metal-alumoxane catalysts such as described in U.S. Patent 4,897,455 of Welborn and U.S. Patent 5,086,025 of Chang and US 5,057,475 of Canich describe catalysts obtained by reacting a transition metal and an alumoxane in the presence of the solid support material. The catalysts are prepared either by reaction of a thermally dehydrated support with alumoxane solution or by the reaction of a hydrated silica gel with an alkylaluminum to generate surface-supported alumoxanes in situ. The supported catalyst may then be employed either as the sole catalyst component or in combination with an organometallic cocatalyst. The supported transition metal-alumoxane catalyst generally produce polymers of lower molecular weight and comonomer incorporation than their unsupported counterpart.

It is known that ionic catalysts are deactivated by Lewis bases. Hence it is a practice not to support ionic catalysts on support materials such as silica.

Supported ionic catalysts containing bis-cyclopentadienyl ("bis-Cp") moieties are described in PCT WO 91/09882. These bis-Cp catalysts provide a supported ionic catalyst for gas or slurry phase olefin polymerization. They are capable of providing a polymer product having a high molecular weight, narrow MWD and CD, good comonomer incorporation, good sequence

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distribution, uniform particles of high bulk density and controlled particle size for ease of removal from the reactor.

It would be desirable to provide a supported ionic catalyst capable of not only producing polymers with the above properties but also include polymers of low density, with optional high molecular weight. Additionally, it would be desirable to produce a catalyst with low hydrogen sensitivity so as to allow use of hydrogen to control molecular weight in, for example, a gas phase polymerization reactor.

SUMMARY OF THE INVENTION

The invention provides a method for preparing supported ionic catalysts which are suitable for use in the polymerization of olefins, diolefins, cyclic olefins and acetylenically unsaturated monomers. The heterogeneous catalyst permit the production of polyolefins of high weight average molecular weight (> 1 million) and narrow MWD at high catalytic activity rates. Moreover, the polyolefin products of the supported catalyst have a narrow CD and improved sequence distribution of comonomers as compared to the products made employing prior art conventional supported Ziegler-Natta catalysts.

The ability to produce a supported ionic catalyst was surprising since it would have been predicted that the reaction of ionic catalyst such as described in EPA 277003 and EPA 277004, with a Lewis base such as is present on a metal oxide surface would result in catalyst deactivation. It was believed that such supports would: 1) decrease catalyst activity due to the residual hydroxyl groups on the surface; 2) bind too strongly to the catalyst through the surface oxide groups; and 3) alter the polymer characteristics.

The supported ionic transition metal catalyst of this invention preferably comprises an ionic transition metal catalyst and a suitable support material. The transition metal component of the ionic catalysts may be selected from a cyclopentadienyl (Cp) derivative of a Group 4 (new IUPAC nomenclature based on Periodic Table of Elements as described in Chemical and Engineering News, 63(5) 27, 1985) metal compound containing at least

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one ligand which will combine with an activator component or at least a portion thereof such as a cation portion thereof. The activator component is an ionic compound comprising a cation which will irreversibly react with at least one ligand contained in said Group 4 metal compound (transition metal component) and an anion which is a chemically stable, non-nucleophilic anionic complex. These can be single coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom or an anion which comprises a plurality of boron atoms such as polyhedral boranes, carboranes, and metallocarboranes.

5 The anions are bulky, typically 4 angstroms or greater, labile and stable to any reaction involving the cation of the activator component. The anion may be any suitably substituted anion which is not hydrolyzed by aqueous solutions. Upon combination of the transition metal component, there is generated an ion pair consisting of a Group 4 metal cation with a formal coordination number of

10 3 or 4 and a valence of +4 and the aforementioned anion, which anion is compatible with and noncoordinating toward the metal cation formed from the transition metal component. The anion of the activator compound must be capable of stabilizing the metal cation complex without interfering with the ability of the metal cation or its decomposition product to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin, cyclic olefin, or an acetylenically unsaturated monomer during polymerization.

15 Likewise if 4 coordination sites of the metal cation are occupied, one must be a ligand sufficiently labile to permit displacement by an olefin, diolefin, cyclic olefin or an acetylenically unsaturated monomer.

25

Independently or together, the transition metal component and the activator are contacted with a dried inorganic or organic solid support material, which preferably has been treated with an aluminum alkyl solution before such contact, to form the supported ionic catalyst which is not deactivated by the

30 Lewis base portions of the supported material. An ionic catalyst of enhanced productivity results when a suitable aluminum alkyl is employed as an additive during polymerization of the olefinic monomer(s). Greater particle size control can also be achieved by prepolymerizing the supported catalyst with olefinic monomer prior to use.

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The method for preparing these supported ionic catalyst comprises the steps of,

(a) combining, in a solvent or diluent

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(i) at least one transition metal component comprising a η^5 -bonded (η =eta) cyclopentadienyl transition metal compound (mono-Cp compound) said metal compound being selected from Group 4 metals,

10

(ii) at least one activator component comprising a cation which will irreversibly react with at least one ligand contained in the Group 4 metal compound and an anion, said anion being a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 angstroms, which may be a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom or comprise a plurality of boron atoms,, said anion being bulky, labile and capable of stabilizing the metal cation formed as a result of reaction between the two, and

15

20

(iii) a catalyst support material which preferably has been dehydrated and treated with a hydrocarbon solution of a hydrolyzable organoadditive, preferably a Group 13 alkyl compound, isolated, washed, and suspended in a suitable solvent,

25

(b) forming a supported catalyst product as a free-flowing solid or slurry.

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The supported catalyst of this invention will polymerize ethylene, α -olefins, diolefins, strained cyclic olefins and/or acetylenically unsaturated monomers either alone or in combination with other olefins and/or other unsaturated monomers in liquid, slurry or gas phase reaction.

35

Optionally, the activator of step (ii) described above may be placed on a support material which has been treated as described and isolated as a supported activator component. The supported activator component may later

be contacted with a transition metal component to form an active catalyst system.

Detailed Description of the Preferred Embodiments

5

The present invention relates to supported mono-Cp catalysts eminently suited for use in various polymerization processes including gas or slurry phase polymerization of olefins. The catalysts preferably include a compound of the Group 4 transition metals, an ionic activator compound and a catalyst support.

10 European Patent Applications EP 277,003, 277,004, PCT International Application WO 92/00333 describe the homogeneous variants of the Group 4 ionic catalysts which are prepared as the reaction product of a Group 4 metal compound and an ionic activator compound.

15

PCT WO 91/09882 describes supported bis-Cp transition metal components activated to catalysts with ionic activators. The present invention differs from that described in WO 91/09882 in that it provides a catalyst capable of producing polymer with low density and optional high molecular weight low density is achieved by the greater ability of these catalyst to

20 incorporate propene and higher alpha-olefins. Because of this ability, larger alpha-olefins than typically used in the gas phase process can be used since the alpha-olefin vapor pressure can be sufficient to yield polymers with relatively low densities. High molecular weight can be obtained due to the low rate of chain transfer even in the presence of alpha-olefins. In addition, the ionically

25 activated mono-Cp catalyst has low hydrogen sensitivity and therefore allows one to use hydrogen to control molecular weight of polymers formed in a continuous or batch gas phase reactor.

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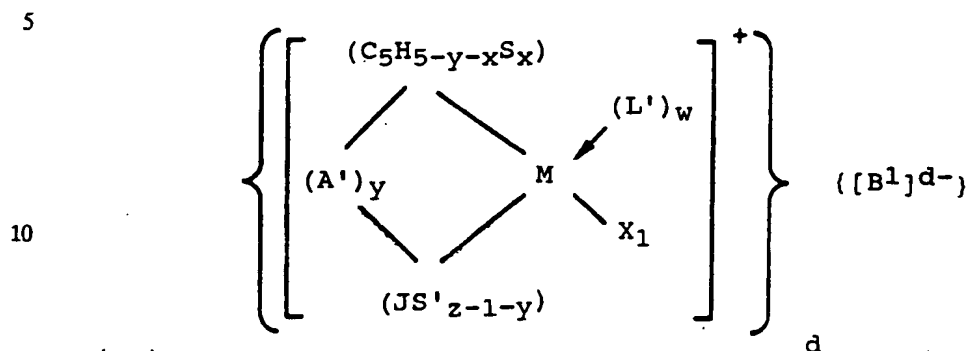
This invention also differs from 91/09882 in that the mono-Cp moieties allow for more pronounced comonomer incorporation and molecular weights in the polymer formed. Since mono-Cp moieties are more open, i.e., less sterically constrained, than bis-Cp compounds, one would expect the mono-Cp compounds to be more easily deactivated by polar units on the support surface than the bis-Cp compounds. Surprisingly, it has been discovered that mono-Cp

35 compounds can be placed on a support with an ionic activator and maintain catalytic abilities.

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Ionic Catalyst System - General Description

The ionic catalysts used in this invention can be represented by the following general formulae:



wherein:

15 A' is a bridging group containing a Group 14 element;

(C₅H_{5-y-x}S_x) is a Cp ring substituted with from zero to five S radicals, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, hydrocarbyl-substituted boron, hydrocarbyl-substituted pnictogen, hydrocarbyl-substituted chalcogen or halogen or two adjacent S groups are joined forming a C₄ to C₂₀ ring to give a saturated or unsaturated polycyclic Cp ligand;

x is from 0 to 5 denoting the degree of substitution;

25 M is a Group 4 transition metal;

L' is a neutral Lewis base;

X₁ is a hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-substituted organometalloid radical which radical may optionally be covalently bonded to both or either M and L' or all and any M, S, and S' and X₁ is not a Cp ring as defined above;

(JS'_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S' is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted

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halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J ;

y is 0 or 1;

w is an integer from 0 to 1;

5 B' is a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 angstroms; and

d is an integer representing the charge of B' .

10 The improved catalysts are preferably prepared by combining at least two components. The first component is a Cp derivative of a Group 4 metal compound containing at least one ligand which will combine with the second component or at least a portion thereof such as a cation portion thereof. The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained in said metal compound
15 (first component) and a non-coordinating anion which is either a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom or an anion comprising a plurality of boron atoms such as polyhedral boranes, carboranes and metallacarboranes.

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The cation portion of the second component may comprise Bronsted acids such as protons, or protonated Lewis bases, or may comprise reducible Lewis acids such as ferricinium, tropylium, triphenylcarbenium or silver cations.

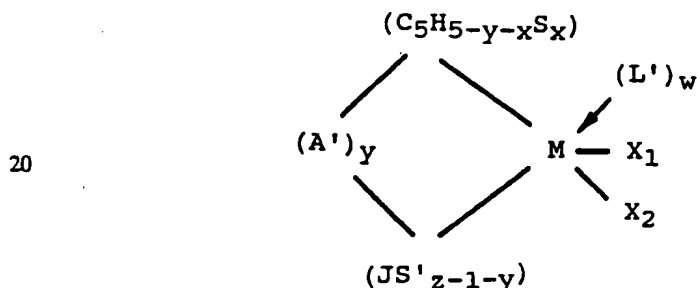
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In general, suitable anions for the second component may be any stable and bulky anionic complex having the following molecular attributes: 1) the anion should have a molecular diameter greater than 4 angstroms; 2) the anion should form stable ammonium salts; 3) the negative charge on the anion should be delocalized over the framework of the anion or be localized within the core
30 of the anion; 4) the anion should be a relatively poor nucleophile; and 5) the anion should not be a powerful reducing or oxidizing agent. Anions meeting these criteria - such as polynuclear boranes, carboranes, metallacarboranes, polyoxoanions and anionic coordination complexes are well described in the literature. Upon combination of the first and second components, the cation of
35 the second component reacts with one of the ligands of the first component, thereby generating an anion pair consisting of a metal cation and the

aforementioned anion, which anion is compatible with and noncoordinating towards the metal cation and the aforementioned anion, which anion is compatible with and noncoordinating towards the metal cation formed from the first component. The anion of the second compound must be capable of
 5 stabilizing the metal cation without interfering with the metal cation's ability to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin, cyclic olefin, or an acetylenically unsaturated monomer during polymerization.

10 A. The Transition Metal Component

The Group 4 metal compounds, useful as first compounds in the preparation of the improved catalyst of this invention are η^5 -cyclopentadienyl transition metal compounds of Group 4 transition metals. In general, useful
 15 transition metal may be represented by the following general formulae:



wherein:

25 L' is a neutral Lewis base;

X₁ is, independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals or X₁ may optionally be covalently bonded to M and L' or all and any M, S, and S'; or two X₁ are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms provided
 30 that X₁ is not a Cp ring as previously defined; and

Examples of bridging groups A' include but are not limited to R₂C, R₂Si, R₂Ge, R₂CR₂C, R₂SiR₂Si, R₂GeR₂Ge, R₂CR₂Si, R₂CR₂Ge, R₂CR₂CR₂C, R₂SiOR₂Si diradicals where R is independently selected from
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the group containing hydride, halogen radicals, and C₁-20 hydrocarbyl radicals. Preferably, A' has a bridge length of two atoms or less as in methylene, ethylene, diphenylsilyl, dimethylsilyl, methylphenylsilyl.

5 Examples of substituent groups S include but are not limited to C₁-20 hydrocarbyl radicals including C₁-20 linear and branched alkyl radicals such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, C₁-20 hydrocarbyl-substituted and unsubstituted cyclic aliphatic and polycyclic aliphatic radicals such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl,
10 phenylcyclohexyl, methylcyclohexyl, cycloheptyl, cyclooctyl, cyclodecyl, cyclododecyl, isopropyldecyl, adamantyl, norbornyl, tricyclo[5.2.1.0]decyl, C₁-20 hydrocarbyl-substituted and unsubstituted aryl radicals including phenyl, methylphenyl, trimethylphenyl, cyclohexylphenyl, naphthyl, butylphenyl, butyldimethylphenyl; C₁-20 substituted hydrocarbyl radicals including benzyl,
15 N,N-dimethylaminobenzyl, N,N-dimethylaminomethyl, methoxymethyl, diphenylphosphinomethyl, fluorophenyl, trifluoromethylphenyl, fluoromethyl, cyanoethyl; C₁-20 linear and branched halocarbyl radicals including trifluoromethyl, perfluoroethyl, perfluoropropyl, perfluorobutyl, perfluorophenyl, chlorodifluoromethyl, chlorotetrafluorophenyl,
20 bromotetrafluorophenyl, iodotetrafluorophenyl; C₁-20 substituted-halocarbyl radicals such as methyltetrafluorophenyl, N,N-dimethyldifluoromethyl, methoxyperfluoroethyl; C₁-20 hydrocarbyl-substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, triphenylsilyl, triphenylgermyl; C₁-20 halocarbyl-substituted organometalloid radicals including
25 tris(trifluoromethyl)silyl, tris(trifluoromethyl)germyl, tris(perfluorophenyl)silyl, tris(perfluorophenyl)germyl; C₁-20 hydrocarbyl-substituted boron radicals including dimethylboranyl, diphenylboranyl; C₁-20 hydrocarbyl-substituted pnictogen radicals including N,N-dimethylamino, diphenylamino, diphenylphosphino, dimethylphosphino; C₁-20 hydrocarbyl-substituted
30 chalcogen radicals including methoxy, ethoxy, butoxy, phenoxy, methylthio, ethylthio, phenylthio, and halogen radicals including fluoro, chloro, bromo, and iodo.

35 Examples of neutral Lewis base ligands (L') include but are not limited to diethylether, dimethylether, N,N-dimethylaniline, trimethylamine, triphenylamine, triethylamine, triphenylphosphine, trimethylphosphine,

thiophene, dimethylsulfide, benzyne, ethylene, propylene, butene, 1,4-hexadiene, acetylene.

X₁ is independently a univalent anionic ligand including but not limited to hydride, C₁-20 hydrocarbyl radicals including C₁-20 linear and branched alkyl radicals such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, C₁-20 hydrocarbyl-substituted and unsubstituted cyclic aliphatic and polycyclic aliphatic radicals such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, phenylcyclohexyl, methylcyclohexyl, cycloheptyl, cyclooctyl, cyclodecyl, cyclododecyl, isopropyldecyl, adamantyl, norbornyl, tricyclo[5.2.1.0]decyl, C₁-20 hydrocarbyl-substituted and unsubstituted aryl radicals including phenyl, methylphenyl, trimethylphenyl, cyclohexylphenyl, butylphenyl, butyldimethylphenyl; C₁-20 substituted hydrocarbyl radicals including benzyl, N,N-dimethylaminobenzyl, N,N-dimethylaminomethyl, methoxyhexyl, diphenylphosphinododecyl, fluorophenyl, trifluoromethylphenyl, fluoromethyl; C₁-20 hydrocarbyl-substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, triphenylsilyl, triphenylgermyl; C₁-20 halocarbyl-substituted organometalloid radicals including tris(trifluoromethyl)silyl, tris(trifluoromethyl)germyl, tris(perfluorophenyl)silyl, tris(perfluorophenyl)germyl. Optionally two X₁ may form a metallocycle with the metal such as methylidene, ethylidene or propylidene. In all cases, X₁ (or both X₁ together) is not a Cp ring as defined by (C₅H₅-y-xS_x).

Examples of S' include but are not limited to C₁-20 hydrocarbyl radicals including C₁-20 linear and branched alkyl radicals such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, C₁-20 hydrocarbyl-substituted and unsubstituted cyclic aliphatic and polycyclic aliphatic radicals such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, phenylcyclohexyl, methylcyclohexyl, cycloheptyl, cyclooctyl, cyclodecyl, cyclododecyl, isopropyldecyl, adamantyl, norbornyl, tricyclo[5.2.1.0]decyl, C₁-20 hydrocarbyl-substituted and unsubstituted aryl radicals including phenyl, methylphenyl, trimethylphenyl, cyclohexylphenyl, naphthyl, butylphenyl, butyldimethylphenyl; C₁-20 substituted hydrocarbyl radicals including benzyl, N,N-dimethylaminobenzyl, N,N-dimethylaminomethyl, methoxymethyl, diphenylphosphinomethyl, fluorophenyl, trifluoromethylphenyl, fluoromethyl, cyanoethyl; C₁-20 linear and branched halocarbyl radicals including

trifluormethyl, perfluoroethyl, perfluoropropyl, perfluorobutyl, perfluorophenyl, chlorodifluoromethyl, chlorotetrafluorophenyl, bromotetrafluorophenyl, iodotetrafluorophenyl; C₁-20 substituted-halocarbyl radicals such as methyltetrafluorophenyl, N,N-dimethyldifluoromethyl, methoxyperfluoroethyl; C₁-20 hydrocarbyl-substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, triphenylsilyl, triphenylgermyl; C₁-20 halocarbyl-substituted organometalloid radicals including tris(trifluoromethyl)silyl, tris(trifluoromethyl)germyl, tris(perfluorophenyl)silyl, tris(perfluorophenyl)germyl.

10

Table 1 depicts representative constituent moieties for the transition metal component. Examples 1 and 2 demonstrate polymerization of ethylene monomers employing a mono-Cp ionic catalyst system.

15

B. The Activator Component

Compounds useful as an activator component in the preparation of the ionic catalyst systems used in the process of this invention comprise a cation, which may be a Bronsted acid capable of donating a proton, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4, 5 or 6 cation) which is formed when the two compounds are combined and said anion will be sufficiently labile to be displaced by olefinic, diolefinic, and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Two classes of compatible non-coordinating anions have been disclosed in EPA 277003 and EPA 277004: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a plurality of boron atoms such as carboranes, metallacarboranes and boranes.

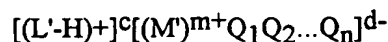
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In general, the activator compounds containing single anionic coordination complexes which are useful in this invention may be represented by the following general formula:



wherein:

H is a hydrogen atom;

5 [L'-H] is a Bronsted acid;

M' is a metal or metalloid;

Q₁ to Q_n are, independently, hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl- and halocarbyl-substituted organometalloid radicals and any one, but not more than one, Q₁ to Q_n may be a halide radical;

m is an integer representing the formal valence charge of M';

and

n is the total number of Q ligands.

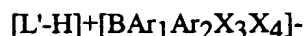
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As indicated above, any metal or metalloid capable of forming an anionic complex which is stable in water may be used or contained in the anion of the second compound. Suitable metals, then, include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.

25

The preferred activator compounds comprising boron may be represented by the following general formula:

30



wherein:

B is boron in a valence state of 3;

Ar₁ and Ar₂ are the same or different substituted-aromatic hydrocarbon radicals containing from about 6 to about 20 carbon atoms and may be linked to each other through a stable bridging group; and

35

X₃ and X₄ are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted pnictogen radicals, substituted chalcogen radicals and halide radicals, with the proviso that X₃ and X₄ will not be halide at the same time.

In general, Ar₁ and Ar₂ may, independently, be any substituted-aromatic hydrocarbyl radical. Suitable aromatic radicals include, but are not limited to, naphthyl and anthracenyl radicals. Suitable substituents on the substituted-aromatic hydrocarbyl radicals, include, but are not necessarily limited to, hydrocarbyl radicals, organometalloid radicals, alkoxy and aryloxy radicals, alkylamido radicals, fluorocarbyl and fluorohydrocarbyl radicals and the like such as those useful as X₃ and X₄. The substituent may be ortho, meta or para, relative to the carbon atoms bonded to the boron atom. When either or both X₃ and X₄ are a hydrocarbyl radicals, each may be the same or a different substituted-aromatic radical as are Ar₁ and Ar₂, or the same may be a straight or branched alkyl, alkenyl or alkynyl radical, a cyclic hydrocarbon radical or an alkyl-substituted cyclic hydrocarbon radical. X₃ and X₄ may also, independently be alkoxy or dialkylamido radicals wherein the alkyl portion of said alkoxy and dialkylamido radicals are hydrocarbyl radicals, organometalloid radicals and the like. As indicated above, Ar₁ and Ar₂ could be linked to either X₃ or X₄. Finally, X₃ and X₄ may also be linked to each other through a suitable bridging group.

Examples of boron compounds which may be used as an activator component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such as trimethylammonium tetra(p-tolyl)boron, trimethylammonium tetra(o-tolyl)boron, tributylammonium tetrakis(pentafluorophenyl)borate, tripropylammonium tetra(o,p-dimethylphenyl)boron, tributylammonium tetra(m,m-dimethylphenyl)boron, tributylammoniumtetra(p-tri-fluoromethylphenyl)boron, tri(n-butyl)ammonium tetra(o-tolyl)boron; dialkyl ammonium salts such as di(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,

Similar lists of suitable compounds containing other metals and metalloids which are useful as activator components may be made, but such

lists are not deemed necessary to a complete disclosure. In this regard, it should be noted that the foregoing list is not intended to be exhaustive and that other useful boron compounds as well as useful compounds containing other metals or metalloids would be readily apparent to those skilled in the art from the foregoing general equations.

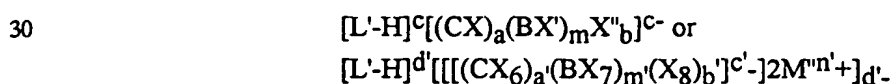
The most preferred activator compounds comprising boron may be represented by the following general formula:



wherein:

F is fluorine, C is carbon and B is boron, L' and Q are as defined above. Illustrative but not limited, examples of most preferred activator compounds comprising boron which may be used in the preparation of the improved catalysts of this invention include N,N-dialkylanilinium salts (L' = N,N-dialkylaniline) where Q is a simple hydrocarbyl such as methyl, butyl, cyclohexyl, or substituted phenyl or where Q is a polymeric hydrocarbyl of indefinite chain length such as polystyrene, polyisoprene, or polyparamethylstyrene. Polymeric Q substituents on the most preferred anion offer the advantage of providing a highly soluble ion-exchange activator component and final ionic catalyst. Soluble catalysts and/or precursors are often preferred over insoluble waxes, oils, phases, or solids because they can be diluted to a desired concentration and can be transferred easily using simple equipment in commercial processes.

Activator components based on anions which contain a plurality of boron atoms may be represented by the following general formulae:



wherein:

[L'-H] is either H⁺ or a Bronsted acid derived from the protonation of a neutral Lewis base;

X, X', X'', X₆, X₇ and X₈ are, independently, hydride radicals, halide radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals, hydrocarbyl- or halocarbyl- substituted organometalloid radicals;

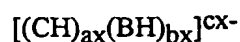
M'' is a transition metal;

5 a and b are integers ≥ 0 ; c is an integer ≥ 1 ; $a + b + c =$ an even-numbered integer from 2 to about 8; and m is an integer ranging from 5 to about 22;

a' and b' are the same or different integer 0; c' is an integer ≥ 2 ; $a' + b' + c' =$ an even-numbered integer from 4 to about 8; m' is an integer from 10 6 to about 12; n' is an integer such that $2c' - n' = d'$; and d' is an integer ≥ 1 .

Preferred anions of this invention comprising a plurality of boron atoms comprise:

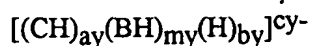
15 (1) A trisubstituted ammonium salt of a borane or carborane anion satisfying the general formula:



20 wherein:

ax is either 0 or 1; cx is either 1 or 2; $ax + cx = 2$; and bx is an integer ranging from about 10 to 12;

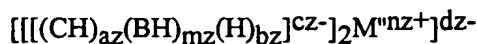
(2) A trisubstituted ammonium salt of a borane or carborane or a 25 neutral borane or carborane compound satisfying the general formula:



wherein:

30 ay is an integer from 0 to 2; by is an integer from 0 to 3; cy is an integer from 0 to 3; $ay + by + cy = 4$; and my is an integer from about 9 to about 18; or

(3) A trisubstituted ammonium salt of a metallaborane or 35 metallocarborane anion satisfying the following general formula:



wherein:

- 5 az is an integer from 0 to 2; bz is an integer from 0 to 2; cz is either 2 or 3; mz is an integer from about 9 to 11; az + bz + cz = 4; and nz and dz are respectively, 2 and 2 or 3 and 1.

Illustrative, but not limited, examples of second components which can be used in preparing catalyst systems utilized in the process of this invention wherein the anion of the second component contains a plurality of boron atoms are mono-, di-, trialkylammonium and phosphonium and dialkylarylammonium and -phosphonium salts such as bis[tri(n-butyl)ammonium]dodecaborate, bis[tri(n-butyl)ammonium]decachlorododecaborate, tri(n-butyl)ammonium dodecachlorododecaborate, tri(n-butyl)ammonium 1-carbadecaborate, tri(n-butyl)ammonium 1-carbaundecaborate, tri(n-butyl)ammonium 1-carbadecaborate, tri(n-butyl)ammonium dibromo-1-carbadecaborate; borane and carborane complexes and salts of borane and carborane anions such as decaborane (14), 7,8-dicarbaundecaborane (13), 2,7-dicarbaundecaborane (13), undecahydride-7,8-dimethyl-7,8-dicarbaundecaborane, tri(n-butyl)ammonium 6-carbadecaborate (12), tri(n-butyl)ammonium 7-carbaundecaborate, tri(n-butyl)ammonium 7,8-dicarbaundecaborate and metallaborane anions such as tri(n-butyl)ammonium bis(nonahydride-1,3-dicarbanonaborato) cobaltate (III), tri(n-butyl)ammonium bis(undecahydride-7,8-dicarbaundecaborato) ferrate (III), tri(n-butyl)ammonium bis(undecahydride-7,8-dicarbaundecaborato) cobaltate (III), tri(n-butyl)ammonium bis(undecahydride-7,8-dicarbaundecaborato)nickelate (III), tri(n-butyl)ammonium bis(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborato)ferrate (III), tri(n-butyl)ammonium bis(tribromooctahydride-7,8-dicarbaundecaborato)cobaltate (III), tri(n-butyl)ammonium bis(undecahydridodicarbasdodecaborato) cobaltate (III) and bis[tri(n-butyl)ammonium] bis(undecahydride-7-carbaundecaborato)cobaltate (III). A similar list of representative phosphonium compounds can be recited as illustrative second compounds, but for the sake of brevity, it is simply noted that the phosphonium and substituted-phosphonium salts corresponding to the listed ammonium and substituted-ammonium salts could be used as second compounds in the present invention.

A. Choice of Transition Metal-Activator Pairs

In general, while most transition metal components identified
5 above may be combined with most activator components identified above to
produce an active olefin polymerization catalyst, it is desirable for continuity of
the polymerization operations that either the metal cation initially formed from
the transition metal component or a decomposition product thereof be a
relatively stable catalyst. It is also desirable that the anion of the activator
10 compound be stable to hydrolysis when an ammonium salt is used. Further, it
is desirable that the acidity of the activator component be sufficient, relative to
the transition metal component to facilitate the needed proton transfer. In
general, Cp metal compounds which can be hydrolyzed by aqueous solutions
are considered suitable as components to form the catalysts described herein.

15

With respect to the combination of the transition metal component with
the activator component to form a catalyst of this invention, it should be noted
that the two compounds combined for preparation of the active catalyst must be
selected to avoid transfer of a fragment of the anion, particularly an aryl group,
20 to the metal cation, thereby forming a catalytically inactive species. This can
be done by steric hindrance, resulting from substitutions on the Cp carbon
atoms as well as substitutions on the aromatic carbon atoms of the anion. It is
followed, then, that the transition metal components comprising
perhydrocarbyl-substituted Cp radicals could be effectively used with a broader
25 range of activator compounds than could transition metal components
comprising unsubstituted Cp radicals. As the amount and size of the
substitutions on the Cp radicals are reduced however, more effective catalysts
are obtained with activator compounds containing anions which are more
resistant to degradation, such as those with substituents on the ortho positions
30 of the phenyl rings. Another means of rendering the anion more resistant to
degradation is afforded by fluorine substitution, especially
perfluorosubstitution, in the anion. Fluoro-substituted stabilizing anions may,
then, be used with broader range of metal compound (first components).
Activators in which the anions comprise pentafluorophenyl groups are
35 preferred for preparing ion-pair transition metal catalysts of this invention. It is

preferred that the mole ratio of transition metal component to activator component be 1:1 or greater.

While generally an activator will be combined with a transition metal compound and be placed on a support, it is possible to place the activator, alone, on a support media. A transition metal compound may be combined with the supported activator at a later point when the catalyst system is to be employed.

10 The Catalyst Support

Typically, the support can be any of the known solid catalyst supports, particularly porous supports, such as talc, inorganic oxides, and resinous support materials such as polyolefins. Preferably, the support material is an inorganic oxide in particulate form.

Suitable inorganic oxide materials which are desirably employed in accordance with this invention include Group 2, 3, 4, 13, or 14 metal oxides. The most preferred catalyst support materials include silica, alumina, and silica-alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania, zirconia. Other suitable support materials, however, can be employed, for example, finely divided polyolefins such as finely divided polyethylene.

The specific particle size, surface area and pore volume of the inorganic oxide determine the amount of oxide that is desirable to employ in preparing the catalyst compositions, as well as affecting the properties of the polymer formed. These properties must frequently be taken into consideration in choosing an inorganic oxide for use in a particular aspect of the invention. In general, optimum results are usually obtained by the use of inorganic oxides having an average particle size in the range of about 0.1 to 600 microns, preferably about 0.3 to 80 microns; a surface area of about 50 to 1,000 square meters per gram, preferably about 100 to 400 square meters per gram; and a pore volume of about 0.5 to 3.5 cc per gram; preferably about 0.5 to 2 cc per gram.

The inorganic oxide support used in the preparation of the catalyst may be any particulate oxide or mixed oxide such that it is substantially free of adsorbed moisture or surface hydroxyl groups. If a support is employed that contains surface hydroxyl groups, a drying or dehydration treatment must be employed. Timing for the dehydration of the support is not critical; i.e., dehydration may occur immediately before use of the support or days before provided once the support is dehydrated, it is protected from moisture and impurities. Thermal treatment to dehydrate the support may be carried out in vacuum or while purging with a dry inert gas such as nitrogen at a temperature of 100°C to 1000°C, and preferably, above 300°C to 900°C, or more preferably 500°C to 850°C. Pressure considerations are not critical. The duration of the thermal treatment can be from 1 to 24 hours.

Chemical dehydration or chemical treatment to dehydrate the support may be accomplished by slurring the inorganic particulate material, such as, for example, silica in an inert low boiling hydrocarbon, such as, for example, hexane. During the chemical dehydration reaction, the support, preferably silica, should be maintained in a moisture and oxygen-free atmosphere. To the silica slurry is then added a low boiling inert hydrocarbon solution of the chemical dehydrating agent. Useful chemical agents are for example, chlorosilanes, such as trimethylchlorosilane and alkyl metal compounds such as dibutylmagnesium, diethylzinc, trimethylaluminum, triethylaluminum, trimethylaluminum and triethylaluminum being particularly preferred. The ratio of millimoles of metal alkyl per gram of support may be between 0.1 to 100, a ratio of 1 to 10 being preferred. The chemical dehydration may be carried out at temperatures of -100°C to 300°C (preferably 0°C to 100°C) and contact times can range from 1 minute to 48 hours, preferably 15 minutes to 2 hours. The treated silica is filtered off and washed with a light aliphatic hydrocarbon (pentanes or hexanes) before drying in vacuo or in a dry stream of inert gas. Since even small amounts of alkyl metal can have an adverse effect on catalyst reactivity to comonomers, the support is washed several times with an inert hydrocarbon solvent to remove both excess dehydration agent and its dehydration reaction products.

To achieve a more active catalyst system the dried support material is subsequently stirred in a hydrocarbon solution of a hydrolyzable organoadditive, preferably a Group 13 alkyl compound such as an alkyl aluminum, such as triethylaluminum (TEAL), preferably 3 mmol or less of 1M
5 hexane solution per gram of support isolated, and washed with a hydrocarbon solvent, such as pentane, to remove unreacted alkyl aluminum. The catalyst system is placed on the support after the treatment with an alkyl aluminum solution.

10 Producing the supported ionic catalyst was surprising since it would have been expected that the reaction of the ionic catalyst with a Lewis base, as present on the oxide surface, would result in catalyst deactivation. The metal oxides generally contain surface hydroxyl groups which typically react with and deactivate the ionic transition metal catalyst. As such it was found that failure
15 to employ a sufficiently dehydrated or dried oxide support would cause catalyst activity to be either greatly diminished or totally absent. Therefore, to achieve a catalytically active system, the inorganic oxide support must be substantially free of adsorbed hydroxyl groups on its surface.

20 The process described herein may also be applied to transition metal components with multiple Cp radicals to achieve the unexpected benefits found for the currently described compositions.

Generally, hydrogen is employed during polymerizations to control MW
25 of a resulting polymer. Certain catalysts in a gas phase reactor have been found to produce hydrogen which must then be released from the reactor. Mono-Cp, ionically activated catalysts offer the potential to use hydrogen as a source of MW control. Mono-Cp ionically activated catalysts generally produce homo- or copolymers having a MW from 2×10^5 to 2×10^6 or greater, optionally having
30 a density range of 0.88-0.97, preferably 0.885-0.960.

Catalyst Preparation and Use

35 The supported ionic transition metal catalyst of this invention may be prepared by combining the transition metal component, the activator component and the support in suitable solvents in one or more steps.

A. Catalyst Preparation

5 The supported catalyst of this invention can be prepared by combining the transition metal, activator components and support in one or more suitable solvents or diluent. Suitable solvents and/or diluents include, but are not necessarily limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, 10 methylcycloheptane; and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene.

It is preferred that the catalyst components be handled in an inert, moisture-free, oxygen-free environment such as argon, nitrogen or helium 15 because of the sensitivity of the catalyst components to moisture and oxygen.

In a preferred method, the transition metal and activator components are combined in a first step in an aromatic solvent to produce a reaction product solution. This reaction may be carried out in the temperature range - 20 100° to 300°C, preferably 0° to 100°C. Holding times to allow for the completion of the reaction may range from 10 seconds to 60 minutes depending upon variables such as a reaction temperature and choice of reactants.

25 The solution produced by combining the transition metal and activator components is then contacted with the support which has been preferably dehydrated at 500° to 850°C, treated with a solution of an alkyl aluminum reagent and subsequently isolated from the wash containing the reagent and its reaction products. The method of contact may vary, but it is preferred that the 30 transition metal/activator solution be added to a rapidly stirred slurry of the catalyst support in a hydrocarbon solvent, preferably an aliphatic solvent, such as pentane.

In a second preferred method, the activator component and support, 35 which has been treated as above, are slurried in a suitable solvent, preferably an aromatic solvent. To this suspension is added a solution of transition metal in

an aliphatic or aromatic solvent, preferably toluene. After holding the reaction for a sufficient period to allow completion of the reaction between the transition metal and activator components, the solvent is evaporated to give the supported catalyst as a free-flowing solid.

5

In a third preferred method, which leads to a more active catalyst, the activator component is dissolved in an aromatic solvent with the support, which has been treated as described above, to produce a supported activator component. This reaction is carried out at a temperature sufficient to produce a homogeneous solution of the activator component, preferably between 25°C to 200°C. The aromatic solvent is then removed to leave a free-flowing supported material. The supported material is subsequently contacted with the transition metal component, preferably in an aliphatic solvent to produce the supported catalyst.

15

Regardless of the method, the active supported catalyst can be recovered by removal of the solvent to obtain a free-flowing solid or alternatively, the active supported catalyst can be maintained in a slurry state for direct use.

20

Contact temperatures may range from 0° to 100°C depending upon the solvents used. Contact times may vary from 10 seconds to 60 minutes.

In the preparation of the supported catalyst, the reagents should be combined to provide a catalyst concentration (transition metal and activator) on the support of from 0.01 wt % to 20 wt %, preferably 1 wt % to 5 wt % based upon the weight of the support.

In an embodiment of the present invention, $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NC}_{12}\text{H}_{23})\text{TiMe}_2$ ($\text{C}_{12}\text{H}_{23}$ is cyclododecyl) or $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrMe}_2$ is reacted with N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron and then contacted with a previously treated alumina, silica or silica-alumina support to produce the catalyst of the present invention. The transition metal and activator components are combined at a temperature within the range -100° to 300°C, preferably from about 0°C to 100°C, and preferably in an aromatic hydrocarbon solvent, most preferably

toluene. A nominal holding time within the range from 10 seconds to 60 minutes will be sufficient before the mixture is contacted with a slurry of the dried support material in an aliphatic solvent for a contacting period of from 10 seconds to 60 minutes.

5

In a second embodiment of the present invention, the silica, alumina, or silica-alumina support, thermally and/or chemically dehydrated as described above, is slurried with N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron preferably in an aromatic hydrocarbon solvent, most preferably toluene. To this
10 slurry is added a solution of the transition metal component in, preferably, toluene. After a contacting period of from 1 to 60 minutes, the solvent is evaporated away in vacuo to recover the supported catalyst.

In a third embodiment of the present invention, in a first step, N,N-
15 dimethylanilinium tetrakis(pentafluorophenyl)boron is dissolved in an aromatic solvent maintained at a temperature sufficient to dissolve the activator component. The support, thermally and/or chemically dehydrated as above, is slurried therein and the activator and support are reacted for 1 minute to 1 hour to produce a supported activator component. The aromatic solvent is removed
20 to leave a free-flowing support material containing the activator component. This supported activator component is then contacted with the transition metal component, preferably in an aliphatic solvent to produce the supported catalyst.

With any of these methods, the active supported catalyst can be
25 recovered by removal of the solvent to obtain a free-flowing solid or, alternately, the active supported catalyst can be maintained in a slurry state for direct use.

A particularly surprising feature of the present invention is that the
30 supported catalyst systems retain most of their catalytic activity over much longer periods of time than their unsupported variants.

The supported catalyst may optionally be prepolymerized with an olefinic monomer in order to achieve improved particle strength and size and
35 reduced reactor fouling during polymerization.

B. Catalyst Use

The supported ionic catalyst may be used to polymerize α -olefins, diolefins, strained cyclic olefins, and/or acetylenically unsaturated monomers
5 alone in combination with other unsaturated monomers. While the catalyst is active for this broad range of olefinic monomer feedstock, α -olefins polymerization is preferred, especially the homopolymerization of ethylene or the copolymerization of ethylene with olefins having 3 to 10 carbon atoms.

10 Gas or slurry polymerizations using the inventive supported catalysts may be conducted generally at a temperature in the range of 0° to 160°C or even higher, and under atmospheric, subatmospheric or superatmospheric pressure conditions.

15 A slurry polymerization process can utilize sub- or super-atmospheric pressures and temperatures in the range of -80° to 250°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene, α -olefin, diolefin, cyclic olefin or acetylenically unsaturated comonomer, hydrogen and catalyst are needed.
20 Alkanes and cycloalkanes, such as butane, pentane, hexane, or cyclohexane, are preferred with C₄ to C₁₀ alkanes especially preferred. Preferred solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, and 1-decene.

25 A gas-phase polymerization process utilizes superatmospheric pressure and temperatures in the range of 50° to 120°C. Gas-phase polymerization can be performed in a stirred or fluidized bed of catalyst and product particles in a pressure vessel adapted to permit the separation of product particles from
30 unreacted gases. Thermostated ethylene, comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at a temperature of 50° to 120°C. Polymer product can be withdrawn continuously or semi-continuously at a rate such as to maintain a constant product inventory in the reactor. After polymerization and
35 deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the polymer product can be recovered

directly from the gas phase reactor, freed of residual monomer with a nitrogen purge, and used without further deactivation or catalyst removal. The polymer obtained can be extruded into water and cut into pellets or other suitable comminuted shapes. Pigments, antioxidants, and other additives, as is known in the art, may be added to the polymer.

In a preferred embodiment of the present invention, the transition metal component will be a substituted or unsubstituted mono-Cp metal heteratom containing compound with one or two lower alkyl substituents and/or one or two hydride substituents. The activator component will be a tri-substituted ammonium salt of a fluorinated tetraphenylboron anion or a triphenyl boron anion. Each of the tri-substitutions in the ammonium cation will be the same or a different lower alkyl or aryl radical. By lower alkyl it is meant an alkyl radical containing from 1 to 4 carbon atoms. N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate is particularly preferred.

The catalysts of this invention, in the absence of a chain transfer agent, can lead to the production of extremely high molecular weight polymers, low melt index, and copolymers having relatively narrow molecular weight distributions. In this regard, it should be noted that homopolymers and copolymers having molecular weights from 2×10^5 up to 2×10^6 or higher and molecular weight distributions within the range of 1.5 to 3 can be produced. Employing these catalysts at lower polymerizing temperatures will usually produce polymers of higher molecular weight. However polymerization temperatures of 60°C or greater can produce polyethylene of MW greater than 2×10^5 . Example 1 illustrates use of catalyst to yield polymer having a molecular weight greater than 1 million. In addition, if lower or moderate molecular weights are desired, molecular weight can be controlled with the use of a chain transfer agent such as hydrogen.

30

Polymers formed employing the supported catalyst described herein, either alone or with an organometallic additive have been found to exhibit high strength useful in fibers; fibers which can be spun or gel bond. Generally, the higher molecular weight polymers produce the properties most desirable for fiber usage.

35

Combinations of two or more ionic transition metal catalyst with the support can be employed in order to obtain broader MWD such as up to 15 or greater. Alternatively, two or more separately supported catalysts can be used to obtain broad MWD polymers and copolymers.

5

Transition metal compound precursors providing tacticity control for the stereospecific polymerization of prochiral olefins, propylene, or higher alpha-olefins, exist when A' acts to restrict rotation of Cp ring and/or the Cp ring is of sufficient bulk to restrict rotation such that the appropriate symmetry conditions are satisfied.

10

Preferable prochiral transition metal compounds for the production of isotactic polymers are those where A' is a bridging group and the substituents on Cp are chosen such that 1) the steric difference between Cp and the heteroatom is maximized and 2) the absence of a plane of symmetry through the metal center and the carbon atoms on the Cp and heteroatom which are bonded to A'. For the production of syndiotactic polymers the second condition requires the presence of a plane of symmetry through the metal center and the carbon atoms on the Cp and heteroatom which are bonded to A'. The supported catalysts may be most usefully employed in gas or slurry phase processes, both of which are known to those of skill in the art.

15

20

US 5,153,157 discloses use of a organo additive to enhance production of an unsupported bis-Cp component ionic catalyst system during polymerization. It has been found that the use of an additive or scavenger with the supported ionic catalyst enhances productivity thereof.

25

The advantages of the instant invention will be more readily appreciated by reference to the following illustrative, non-limiting examples.

Example 1 - Teal-Treated Silica - Polyethylene Polymerization

To 5.0 g of Davison 948 silica slurried in pentane, 15 ml of 1.5 M teal was added, and the slurry was stirred for 30 minutes. The silica was then washed eight times with pentane to remove any free aluminum alkyl and then dried in vacuo.

To 1.0 g of teal-treated silica slurried in toluene, 24 mg of [DMAH][B(pfp)₄] and 15 mg of Me₂Si(Me₄C₅)(NC₁₂H₂₃)TiMe₂ dissolved in 15 ml of toluene was added dropwise. After addition, the solvent was removed in vacuo and isolated.

400 ml of hexane, 1.0 g of the supported catalyst, and 200 psi of ethylene were added to the reactor at 60°C and allowed to react for 30 minutes. Polyethylene (20.0 g) was recovered. The molecular weight of this polyethylene could not be determined by gpc since the polymer was not soluble in orthodichlorobenzene at 170°C thus indicating a molecular weight greater than 1 to 2 million. The polymer density was measured at 0.934 g/cc. DSC data gave a second melt at 137°C, a final melting point at 140°C, and a calculated crystallinity of 31%.

Example 2 - Teal-Treated Silica, Polyethylene Polymerization

Silica (Davison 948, dried at 800°C, 100 g) was slurried in pentane (1 l). Triethylaluminum (200 ml of 1.5 M solution in heptane) was added over 30 minutes and the slurry stirred an additional 45 minutes. The solids were filtered off, washed 10 times with pentane and dried. A sample (5 g) was slurried in toluene (30 ml). A solution of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (162 mg) in warm toluene (100 ml) was added slowly. The solvent was evaporated in vacuo.

A sample of the support thus treated (500 mg) was slurried in pentane and dimethylsilyl(tetramethylcyclopentadienyl)(t-butylamido)zirconium dimethyl (8 mg) in pentane solution added. The solvent was evaporated in vacuo to afford the supported catalyst.

5 The supported catalyst (420 mg) was transferred, under nitrogen, to a 1 liter stainless-steel autoclave which had previously been flushed with nitrogen and which contained 400 ml of dry, deoxygenated hexane. The autoclave was pressured to 100 psi with ethylene and stirred at 60°C. After 10 minutes, the autoclave was cooled, vented, and the contents separated by filtration. The yield of polyethylene was 11.0 g.

10 Although the invention has been described with reference to its preferred embodiments, those of ordinary skill in the art, upon reading this disclosure, will appreciate changes and modifications which do not depart from the scope and spirit of the invention as described above or claimed hereafter.

TABLE 1

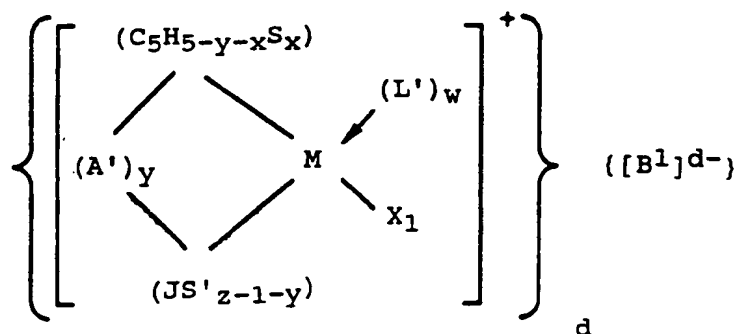
A'	(C ₂ H ₅ -v-x ₂ x)	(JS' z)	X ₁	M
dimethylsilyl	cyclopentadienyl	t-butylamido	hydride	zirconium
diethylsilyl	methylcyclopentadienyl	phenylamido	methyl	hafnium
di-n-propylsilyl	1,2-dimethylcyclopentadienyl	p-n-butylphenylamido	ethyl	titanium
di-isopropylsilyl	1,3-dimethylcyclopentadienyl	cyclohexylamido	phenyl	
di-n-butylsilyl	indenyl	perfluorophenylamido	n-propyl	
di-t-butylsilyl	1,2-diethylcyclopentadienyl	n-butylamido	isopropyl	
di-n-hexylsilyl	tetramethylcyclopentadienyl	methylamido	n-butyl	
methylphenylsilyl	ethylcyclopentadienyl	ethylamido	amyl	L'
ethylmethylsilyl	n-butylcyclopentadienyl	n-propylamido	hexyl	ethylene
diphenylsilyl	cyclohexymethylcyclopentadienyl	isopropylamido	isobutyl	propylene
di(p-t-butylphenylsilyl)	n-octylcyclopentadienyl	benzylamido	heptyl	1-butene
n-hexylmethylsilyl	beta-phenylpropylcyclopentadienyl	cyclododecylamido	octyl	1,4-hexadiene
cyclopentamethylenesilyl	tetrahydroindenyl	t-butylamido	nonyl	1,3-butadiene
cyclohexamethylenesilyl	propylcyclopentadienyl	t-butylphosphido	decyl	1,3-hexadiene
cyclooctamethylenesilyl	t-butylcyclopentadienyl	ethylphosphido	cetyl	acetylene
dimethylgermanyl	benzylcyclopentadienyl	phenylphosphido	methylidene (both X)	methylacetylene
diethylgermanyl	diphenylmethylcyclopentadienyl	cyclohexylphosphido	ethylidene (both X)	ethylacetylene
phenylamido	trimethylatannycyclopentadienyl	oxo	propylidene (both X)	benzynes
t-butylamido	trimethylplumbylcyclopentadienyl	sulfido		diethylether
methylamido	triethylplumbylcyclopentadienyl			dimethylether
t-butylphosphido	trifluoromethylcyclopentadienyl			trimethylamine
ethylphosphido	trimethylsilylcyclopentadienyl			triphenylamine
phenylphosphido	pentamethylcyclopentadienyl (when y=0)			triethylamine
methylene	fluorenyl			triphenylphosphine
dimethylmethylene	octahydrofluorenyl	JS' z-1-y (y=0)		tetrahydrofuran
diethylmethylene	N,N-dimethylamidocyclopentadienyl	methoxide		thiophene
thylene	dimethylphosphidocyclopentadienyl	methythio		dimethylsulfide
dimethylethylene	methoxycyclopentadienyl	ethylthio		
dipropylethylene	(N,N-dimethylamidomethyl) cyclopentadienyl	dimethylamido		
		diphenylphosphido		

WHAT IS CLAIMED IS:

- 1 1. A method for preparing a supported ionic catalyst comprising
2 the steps of:
3 (a) combining,
4 (i) at least one transition metal component comprising a
5 monocyclopentadienyl metal compound, said metal compound including a
6 metal being selected from Group 4 transition metals;
7 (ii) at least one activator component comprising a cation
8 which will irreversibly react with at least one ligand contained in said metal
9 compound and an anion, said anion being a chemically stable non-nucleophilic
10 anionic complex;
11 (iii) a catalyst support material; and
12 (b) optionally prepolymerizing said supported catalyst system
13 with an olefinic monomer.
- 1 2. The method of claim 1 wherein the support has been treated
2 with a hydrocarbon solution of a hydrolyzable organoadditive, preferably a
3 Group 13 alkyl compound most preferably triethylaluminum.
- 1 3. The method of claim 2 wherein the support is treated at
2 temperatures of 100°C to 300°C, preferably 0° to 100°C, for 1 minute to 48
3 hours, preferably 15 minutes to 2 hours.
- 1 4. The method of claims 2 or 3 wherein the ratio of millimoles of
2 metal alkyl per gram of support is 0.1 to 100, preferably 1 to 10.
- 1 5. The method of claim 1 or 2 wherein the support has been
2 previously dehydrated.
- 1 6. The method of claim 5 wherein the support is dehydrated at
2 100°C to 1000°C, preferably 300°C to 800°C, most preferably 500°C to
3 850°C, for 1 to 24 hours.
- 1 7. The method of claim 2, 3 or 4 wherein after treatment with the
2 hydrocarbon solution the support is isolated.

8. The method of any preceding claim wherein the supported catalyst is formed as a free flowing solid.

9. The method of claim 1 wherein the ionic catalyst is represented by the following general formulae:



wherein:

A' is a bridging group;

(C₅H_{5-y-x}S_x) is a Cp ring substituted with from zero to five S radicals, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, hydrocarbyl-substituted boron, hydrocarbyl-substituted pnictogen, hydrocarbyl-substituted chalcogen or halogen or two adjacent S groups are joined forming a C₄ to C₂₀ ring to give a saturated or unsaturated polycyclic Cp ligand;

x is from 0 to 5 denoting the degree of substitution;

M is Group 4 transition metal;

L' is a neutral Lewis base;

X₁ is a hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-substituted organometalloid radical, which radical may optionally be covalently bonded to both or either M and L' or all and any M, S, and S' and X₁ is not a Cp ring as defined above;

(JS'_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S' is a radical group

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33 which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted
34 halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted
35 organometalloid; and z is the coordination number of the element J;

36 y is 0 or 1;

37 w is an integer from 0 to 1;

38 B' is a chemically stable, non-nucleophilic anionic complex having a
39 molecular diameter about or greater than 4 angstroms; and

40 d is an integer representing the charge of B'.

1 10. The method of any preceding claim wherein said support is
2 selected from alumina, silica, alumina-silica, talc, magnesia, zirconia, titania,
3 finely divided polyolefins or mixtures thereof, preferably alumina, silica, or
4 mixtures thereof.

1 11. The method of claim 9 wherein $(C_5H_5-y-xS_x)$ is
2 tetramethylcyclopentadienyl, A' is dimethylsilyl, y is 1, (JS'_{z-1-y}) is t-
3 butylamido, M is zirconium, X1 is methyl, L' is N,N-dimethylaniline, and B' is
4 tetrakis(pentafluorophenyl)-borate.

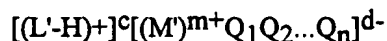
1 12. The method of claim 11 wherein (JS'_{z-1-y}) is $C_{12}H_{23}$, M is
2 titanium.

1 13. The method of claim 9, wherein the at least one transition metal
2 component and the at least one activator component are first reacted in a
3 solvent or diluent and the direct product or the decomposition product of said
4 direct product is contacted in a suitable solvent with the catalyst support
5 material and optionally prepolymerizing with an olefinic monomer.

1 14. The method of claim 9, wherein the activator component is
2 dissolved in an aromatic solvent and the support is slurried therein and allowed
3 to react, the supported activator component is then contacted with the
4 transition metal component in an aliphatic or aromatic solvent and optionally
5 prepolymerizing with an olefinic monomer.

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1 15. The method of claim 9 wherein B' is represented by the general
2 formula:



3
4
5
6 wherein:

7 H is a hydrogen atom;

8 [L'-H] is a Bronsted acid;

9 M' is a metal or metalloid;

10 Q₁ to Q_n are, independently, hydride radicals, bridged
11 or unbridged dialkylamido radicals, alkoxide and aryloxy radicals,
12 substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl
13 radicals and hydrocarbyl- and halocarbyl-substituted organometalloid
14 radicals and any one, but not more than one, Q₁ to Q_n may be a halide
15 radical;

16 m is an integer representing the formal valence charge of

17 M'; and

18 n is the total number of Q ligands.

1 16. A catalyst for the polymerization of α -olefins, diolefins, strained
2 cyclic olefins, and/or acetylenically unsaturated monomers alone in combination
3 with other unsaturated monomers obtained by the method of any preceding
4 claims.

1 17. A process to produce polyolefins comprising contacting
2 α -olefins, diolefins, strained cyclic olefins, and/or acetylenically unsaturated
3 monomers alone in combination with other unsaturated monomers under
4 polymerization conditions in the presence of the catalyst obtained by any of the
5 methods of claim 1 to 13.

1 18. The process according to claim 17 wherein a hydrolyzable
2 organoadditive, preferably a Group 13 metal compound, most preferably
3 triethylaluminum is employed.

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- 1 19. The process according to claim 17 or 18 wherein the
2 polymerization conditions comprise temperatures from -80°C to 250°C and
3 pressures from 0.1 atm. to 3500 atm.
- 1 20. The process according to claims 17, 18, or 19 wherein at least 2
2 transition metal components are employed during polymerization.
- 1 21. The process of claim 20 wherein an organoadditive is employed
2 during polymerization.
- 1 22. The process of claim 17, 18, 19, 20, or 21 wherein hydrogen is
2 employed during polymerization.
- 1 23. The process of claim 22 wherein hydrogen is employed in a
2 continuous gas phase polymerization process to obtain a polymer having high
3 molecular weight.
- 1 24. The process of claims 17, 18, 19, 20 or 21 wherein the
2 polyolefin product formed has a weight average molecular weight of 2×10^5 or
3 greater.
- 1 25. The process of claim 24 wherein the polyolefin formed has a
2 density in the range of 0.88 to 0.97, preferably 0.885 to 0.960.
- 1 26. The process of claim 17, 18, 19, 20, or 21 wherein the
2 polyolefin formed is made into a fiber.
- 1 27. A method for preparing a supported activator component
2 comprising combining cation which is capable of irreversibly reacting with at
3 least one ligand contained in a mono-cyclopentadienyl transition metal
4 component and an anion, said anion being a chemically stable, non-nucleophilic
5 anionic complex having a molecular diameter about or greater than 4
6 angstroms, and a catalyst support material.

INTERNATIONAL SEARCH REPORT

PCT/US 93/07352

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08F4/64; C08F4/02; C08F10/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,X	EP,A,0 522 581 (IDEMITSU) 13 January 1993 see claims 1-9 see page 4, line 7 - line 28 see tables 1-3	1-8
A	WO,A,9 109 882 (EXXON) 11 July 1991 cited in the application see the whole document	1
A	EP,A,0 406 912 (MITSUI) 9 January 1991 see the whole document	1
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
12 OCTOBER 1993		21. 10. 93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		DE ROECK R.G.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9307352
SA 77945

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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